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AN EXPERIMENTAL DETERMINATION OF THE ABSOLUTE OSCILLATOR STRENGTHS OF THE LINES OF TWO N II SUPERMULTIPLETS

By Frithjof Mastrup

Translation of "Eine experimentelle Bestimmung der absoluten Oszillatorenstärken der Linien zweier N II-Supermultipletts."
Inaugural dissertation on reaching the degree of
Doctor of the Higher Philosophy Faculty,
Christian-Albrechts-University
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CONTENTS

Abstract:

The following work describes the experimental determination of the absolute oscillator strengths of several N II-lines. The light source was the plasma of a wall-stabilized enclosed [cylindrical] arc in pure nitrogen. The parameters of this plasma near the axis of the arc were calculated from the measured total intensity of the hydrogen-like triplet-multiplet of the series 2p3d-2p4f. It was here assumed that the oscillator strengths of this multiplet can be calculated by the Bates and Damgaard Coulomb field approximation.

In addition, an attempt was made to check the measured oscillator strengths of the N II line in the nitrogen plasma by measurements in a helium-nitrogen mixture, using the known oscillator strengths of helium.

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I. Method

The relation between the absorbtion oscillator strength and the intensity J of a spectral line emitted from an optically thin layer is

$$f_{mn} = 9.491 \cdot 10^{16} \frac{J}{l} \frac{\lambda^3}{n_r} \frac{Z_r}{g_n} e^{\frac{\chi_m}{kT}} \qquad [8, 15]$$

where:

f_{mn} = the absorption oscillator strength.

l = the emitting layer length in centimeters.

Z_r = the partition function.

n_r = the total particle density in the ionization level in question.

J = the total intensity in ergs per square centimeter per second per steradian.

λ = the wavelength in centimeters.

χ_m = the excitation energy in ergs.

T = the temperature.

The subscript m refers to the higher level.

As well as the intensity of the lines under investigation, we must know the temperature and the particle density in the plasma. In our method, the Saha equation, the quasi-neutrality condition and the known total pressure are used to relate the intensity measurements on lines of known oscillator strength to the determination of all these parameters.

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II. The Light Source

A light source intended for the measurement of absolute oscillator strengths must meet the following specifications:

1. The lines must be emitted from an optically thin layer.
2. The radiation intensity from the area of plasma being observed must not change during the measurement.
3. The geometrical thickness of the observed layer must be measurable.
4. The light source must be in thermal equilibrium.

Quasi-neutrality is also required, but this is obtained in all arcs used as light sources [8]. By special construction of the arc it is possible to make the total pressure of the plasma equal to the pressure of the surrounding atmosphere.

We will now consider whether these specifications are met by a wall-stabilized enclosed arc (see section 3). The arc was filled either with pure nitrogen, or, in order to compare the nitrogen lines under investigation with helium lines, with a mixture of nitrogen and helium. A preliminary investigation gave for the temperature on the axis of the arc about 20,000 degrees in both cases, under the desired experimental conditions. This gives for the electron density in the pure nitrogen plasma $n_e = 1.8 \cdot 10^{17}$ per cc.

1. The low optical thickness of the layer from which the light is emitted can be easily checked, when we remember that the intensity distribution in the line follows the Doppler distribution. If the layer optical thickness in the line center is $C = k_0 \cdot l \ll 1$ for the Doppler broadened line, this relation is only valid for the true profile.

We have

$$C' = 4.99 \cdot 10^{-13} \frac{\lambda_0^2}{\Delta\lambda_D} \cdot N_n f_{mn} l \qquad [15]$$

with

k_0 = the absorption coefficient at the line center,

l = the geometrical emitting layer length,

N_n = the number of particles in the lower state,

$\Delta\lambda_D$ = the Doppler width.

For nitrogen at 20,000 degrees, $\Delta\lambda_D/\lambda_0 = 1.62 \cdot 10^{-5}$. The experimental conditions were so chosen that, at the worst, C = 0.3. Assuming a Doppler line profile, this corresponds to an intensity loss of 10%. However, the true line profile has much lower absorption losses. For the majority of the lines investigated, the calculated C-values lay much below 0.1, so that with them self-absorption was not important.

The helium lines investigated showed such a strong broadening, caused by the high electron density, that for them also a thin emitting layer applied. For the $2^3P - 3^3D$ helium line at λ = 5876 Å, a half width $2\Delta\lambda$ = 4 Å was measured, contrasting with a calculated value of $2\Delta'\lambda$ = 0.3 Å, assuming a Doppler profile.

2. The arc stability. Water-stabilized arcs burn very unstably [4]. Wall-stabilized arcs are free from this disadvantage, and must therefore be used for measurements of absolute oscillator strengths.

In the case where the excitation energies of the lines investigated are close, the instability of the water-stabilized arc does not disturb relative measurements of oscillator strengths. This arc was therefore used for the relative measurements on some N II lines, when the wall-stabilized arc did not give a sufficiently low optical thickness.

The arc current was kept constant during the measurements.

3. To utilize the most homogeneous emitting layer possible, end-on observations were made. The angular aperture used with an arc can always be made so small that light only from the immediate neighborhood of the axis of the arc reaches the slit. The angular apertures used lay between 1/80 and 1/150.

The check on the emitting layer geometrical length is made with side-on viewing. Here it was seen that the N II lines were emitted only from the region of the discharge column confined by the tube. The length of this tube must therefore be taken as the emitting layer geometrical length.

4. Thermal equilibrium. The fractional difference between the electron temperature and the gas temperature is

$$\frac{T_e - T_g}{T_e} = \frac{m_s}{4m_e} \cdot \left(\frac{\lambda_e eE}{3/2kT}\right) \qquad [8]$$

where m_s is the mass of the nitrogen atom, and m_e is the mass of an electron. When there is a collision between an electron and an ion, we have, approximately,

$$Q_{ei} = \frac{e^4}{(kT)^2} \ln \frac{kT}{e^2 n_i^{1/3}} \qquad [10]$$

where Q_{ei} is the cross section for the collision in question. Since the pure nitrogen plasma at 20,000 degrees is completely ionized, only this ion cross section need be considered. For a temperature of 20,000 degrees and an ion density of $n_i = 1.8 \cdot 10^{17}$ per cc the collision cross section is

$$Q_{ei} = 2.1 \cdot 10^{-14} \text{cm}^2.$$

The electron mean free path is then

$$\lambda_e = 2.5 \cdot 10^{-4} \text{ cm}.$$

The electrical field strength in wall-stabilized arcs can be very easily measured with probes of copper discs. In this way the disturbing contact potential can be eliminated by measurements at two different separations. Under the experimental conditions, the measured value of the field strength was

$$E = 30 \text{ to } 32 \text{ volts/cm.}$$

With these values, we get

$$(T_e - T_g)/T_e = 0.05 = 5\%.$$

That means that the electron temperature, which is controlled by the electron velocity distribution, lies about 5% above the temperature of the heavy particles. Among effects not considered, the spontaneous emission processes are the only ones which reduce this temperature difference. However, from considerations given below, it follows that the number of photo-processes is negligible compared with the number of collisions, so that the spontaneous emission can be ignored.

The ionization temperature T_i [8] is the term used to describe the temperature determined by ionization equilibrium through the Saha equation. According to a calculation made by Elwert [6], the Saha equation is valid only where the electron density is greater than $7 \cdot 10^{15}$ per cm^3. In that case, the ionization collisions and the three-body recombinations are much more frequent than photo-ionization and recombination. Consequently, after using the Saha equation to calculate the electron density for a plasma enclosed in a vessel, if subsequently we suppose the walls of the vessel to be removed, the electron density does not change. We have, therefore, no misgivings about the plasma in our discharge ($n_e = 1.8 \cdot 10^{17}$ per cm^3). It may be asked whether, in the Saha equation, the electron temperature or the gas temperature should be used. That can be decided by estimating the relative frequencies of electron and ion collisions. For the experimental plasma the collision ratio is

$$\frac{\text{electron/ ion collisions}}{\text{ion/ ion collisions}} = 160$$

The electron temperature should therefore be used for the ionization temperature.

The excitation, like the ionization, is predominantly determined by electron collisions. A Boltzmann distribution of excited states is anticipated, if at $T = 20{,}000$ degrees and $\lambda = 4500$ Å, the following inequality is satisfied:

$$3 \cdot 10^7 \frac{n_e Q_{ex}}{A_{nm}}(E_n + kT) \gg 1; \quad (E_n + kT) \text{ in } [EV] \qquad [8]$$

With $Q_{ex} = 10^{-16}$ cm^2, $n_e = 1.8 \cdot 10^{17}$ per cm^3, $A_{nm} = 10^8$ per sec, and $E_n \approx 22.3$ ev, this expression gives a value of 173, so the thermal occupation of the levels can be considered certain. This conclusion is confirmed by considering also the higher excitations.

Summarizing, we can say that under the experimental conditions in the enclosed arc, the electron, ionization and excitation temperatures agree. However, the velocity distribution of the heavy nitrogen atoms corresponds to a gas temperature about 5% lower.

The excitation temperature is given by the intensity of a spectral line, for a known oscillator strength and particle density, if the occupation of the excited states follows a Boltzmann distribution. According to the calculation made in this section, in the present case the excitation temperature agrees with the electron temperature and the ionization temperature.

For our plasma we have shown that

$$T_i = T_e = T_{ex} \quad \text{and} \quad T_g < T_e$$

It now remains to show the importance of the latter departure from thermal equilibrium.

The gas temperature T_g influences the total number of particles in the Dalton partial pressures law, and we must introduce a mean temperature T_m defined by the relation:

$$\frac{p_0}{kT_m} = \frac{p_e}{kT_e} + \frac{p_g}{kT_g}$$

where p_0, p_e and p_g are the total pressure, the electron pressure and the gas pressure respectively. From the equation $p_0 = p_e + p_g$ = const and $T_g = 0.95\,T_e$ we get

$$\frac{T_e}{T_m} = \frac{1.05 + \frac{p_e}{p_g}}{1 + \frac{p_e}{p_g}}$$

Further, since the nitrogen plasma at 20,000 degrees is fully ionized, we have $p_e = 1.05\,p_g$, and so

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$$\frac{T_e}{T_m} = 1.025.$$

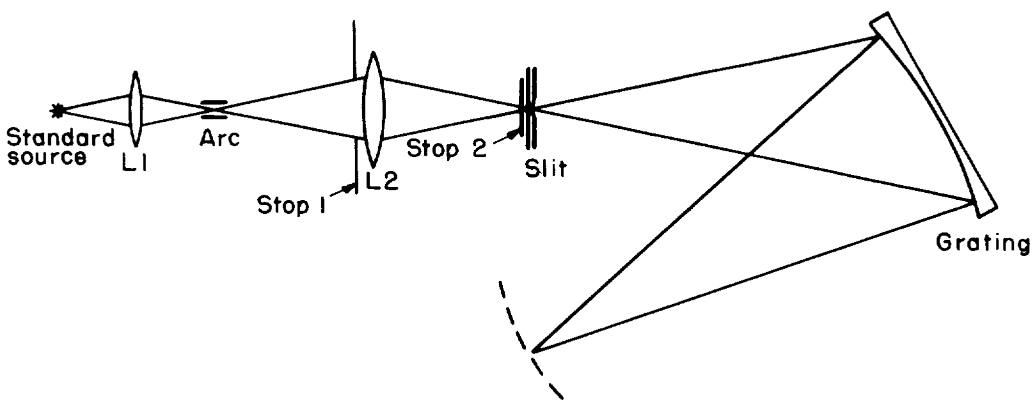
If, instead of the mean temperature, the electron temperature is used for the Dalton law calculation, the total number of particles obtained is lower by about 2.5%. A calculation of errors shows that this produces at the most a 2.5% error in the measured oscillator strength. The difference between T_e and T_m can be neglected, since the spectral line intensity measurements are of considerably lower accuracy than this. Therefore, in spite of the existing departure from thermal equilibrium, it can be considered that not only

$$T_i = T_e = T_{ex}, \text{ but also } T_e = T_g.$$

These considerations apply to a pure nitrogen plasma. If gas mixtures containing very light components such as hydrogen or helium are used, due to the better mass ratios between the helium or hydrogen and the electrons, the fractional temperature difference $(T_e - T_g)/T_e$ will be smaller.

III. The Experimental Procedure

1. Several of the N II multiplets can not be obtained from an optically thin layer in a pure nitrogen plasma in a wall-stabilized enclosed arc. Therefore, several of the relative intensity measurements were made with the water-stabilized arc constructed by H. Motschmann [12, 13], which can be filled with the experimental gas through a nozzle. It is simplest in our case to blow in air. End-on observations were made. To keep the obtained spectrum almost free from carbon and cyanide bands, a compressed air blast was directed close to the



Experimental arrangement

electrodes. A Rowland grating in a Paschen mounting was used, with a second order dispersion of 1.3 A/mm.

Stop 1 kept the angular aperture to 1/80. Stop 2, directly in front of the slit, selected radiation from the axis of the arc, assumed homogeneous. This arrangement is necessary because of the astigmatism of the grating mounting. The Euler standard source [7] was imaged on to the center of the arc by the achromat L_1. The reflection losses in L_1 could be taken into account by measuring the transmission as a function of wavelength.

The Hauff Pancrosin plate with a speed of 17/10 DIN was suitable for the spectral region 4500-6000 Å and the high dispersion available. A three prism spectrograph and a Zeiss step-filter [wedge] were used to calibrate the plates. A wedge was made for each multiplet to avoid errors. To avoid disturbances from the Schwarzschild exponent, the same exposure times are best used for the arc spectrum, the standard source, and the wedge. This can be achieved through appropriate stops or by changing the slit width. A Siemens interval timer ensured the accurate control of the exposure time.

To produce sufficiently strong N II lines an arc current of about 350 amps is necessary. With a total arc voltage of 250 volts, the power consumed is 90 kw.•

The plasma of this arc consists of a mixture of water vapor and air. The ratio of the components is obtained spectroscopically by measuring a line of known oscillator strength for each component. In this way a measurement free from mixing effects that might occur in the arc plasma is obtained.

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By far the best line for hydrogen is H_β. For oxygen it was necessary to fall back on the very uncertain multiplet $3^5S^0-4^5P$ [9], λ = 3947 Å. The N II line used ($3s^3P_1^0 - 3p^3P_0$, λ = 4621 Å) is probably the best in this region.

Their oscillator strengths can be obtained from the data on the absolute measurements described in the next section.

With the two relative intensity measurements $J(0)/J(H)$ and $J(N^+)/J(H)$ and the absolute intensity measurement $J(N^+)/l$ all the parameters for the plasma can be calculated.

The system of equations used is as follows: [14]

$$(1)\quad \frac{n_{H^+}}{n_H} = \frac{1}{n_e}\cdot\frac{(2\pi m_e kT)^{3/2}}{h^3}\cdot e^{-\frac{\chi_H-\Delta\chi}{kT}}; \qquad \Delta\chi = 7\cdot 10^{-7} n_e^{1/3}\cdot(Z_{eff})^{2/3}\,[\text{ev}]$$

$$(Z_{eff} = \text{Effective atomic no.})$$

$$(2)\quad \frac{n_{O^+}}{n_O} = \frac{n_{H^+}}{n_H}\,\frac{2\cdot Z(O^+)}{Z(O)}\cdot e^{-\frac{\chi_O-\chi_H}{kT}};$$

$$(3)\quad \frac{n_{N^+}}{n_N} = \frac{n_{H^+}}{n_H}\,\frac{2\cdot Z(N^+)}{Z(N)}\cdot e^{-\frac{\chi_N-\chi_H}{kT}};$$

$$(4)\quad \frac{n_O}{n_H} = \frac{J(O)}{J(H)}\,\frac{(g_n\cdot f_{mn})^H}{(g_n\cdot f_{mn})^O}\left(\frac{\lambda_O}{\lambda_H}\right)^3\cdot e^{\frac{\chi_m^O-\chi_m^H}{kT}};$$

$$(5)\quad \frac{n_{N^+}}{n_H} = \frac{J(N^+)}{J(H)}\,\frac{(g_n\cdot f_{mn})^H}{(g_n\cdot f_{mn})^{N^+}}\left(\frac{\lambda_{N^+}}{\lambda_H}\right)^3\cdot e^{\frac{\chi_m^{N^+}-\chi_m^H}{kT}};$$

$$(6)\quad n_{N^+} = \frac{J(N^+)}{l}\cdot 9.491\cdot 10^{16}(\lambda_{N^+})^3\cdot\frac{Z(N^+)}{(g_n\cdot f_{mn})^{N^+}}\cdot e^{\frac{\chi_m^{N^+}}{kT}};$$

$$(7)\quad \frac{P_O}{kT} \doteq 2n_e + n_O + n_H + n_N; \qquad P_O = 1.013\cdot 10^6\,\text{dyn/cm}^2$$

$$(8)\quad n_e = n_{H^+} + n_{O^+} + n_{N^+}$$

In Equation (6) the wavelength must be in centimeters. The lowering of the ionization energy $\Delta\chi$ was taken from a paper of A. Unsoeld [14].

When the temperature has been determined through the solution of this system of equations, a large number of N II lines can be calculated through relative intensity measurements. If f^I and f^{II} are the oscillator

•The Deutsche Forschungsgemeinschaft [German Research Society] obligingly put a Brown Boveri rectifier unit at our disposal.

strengths of two N II lines, and J^I/J^{II} their measured intensity ratio, their ratio of oscillator strengths is

$$\frac{f^{I}_{mn}}{f^{II}_{mn}} = \frac{J^{I}}{J^{II}} \cdot \left(\frac{\lambda^{I}}{\lambda^{II}}\right)^{3} \cdot \frac{g^{II}_{n}}{g^{I}_{n}} \cdot e^{\frac{\chi^{I}_{m}-\chi^{II}_{m}}{kT}}$$

2. The absolute oscillator strengths of the N II lines can be obtained by relating them to the multiplet of the 3d-4f series. We have several grounds for believing that the Coulomb field approximation is perfectly valid for these transitions. The electron configuration of the N II atom in the states in question are

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$$1s^2\, 2s^2\, 2p\, 3d \text{ and } 1s^2\, 2s^2\, 2p\, 4f$$

Thus, the valency electron is relatively far from the doubly ionized atomic residue. We expect, therefore, a great resemblance to hydrogen, both in the 3d and 4f terms and in the corresponding lines. This is in fact found. The effective main quantum numbers are almost integral:

3d: 2.90 to 3.00 4f: 3.97 to 4.00

In addition, these transitions are widely different from the usual N II lines in their very diffuse appearance. Finally, the results of the present work also make it clear that the method of Bates and Damgaard [3] for the computation of the absolute oscillator strengths is particularly appropriate for this multiplet.

The computation gives for the absolute line intensities:

TABLE I

p · d \ p · f	^3G	^3F	^3D	^1G	^1F	^1D
^3F	231	20.4	0.56			
^3D		173	20.8			
^3P			126			
^1F				95.7	9.98	0.20
^1D					67.0	6.20
^1P						43.9

The total line intensity of the triplet-supermultiplet:

$$S_{total} = 571.8 \text{ A.U.}$$
$$S(^3F\text{-}^3G) + S(^3D - {}^3F) + S(^3P\text{-}^3D) = 530 \text{ A.U.}$$

Oscillator strengths:

p · d \ p · f	^3G	^3F	^3D	^1G	^1F	^1D
^3F	0.828	0.0724				
^3D		0.828	0.101			
^3P			0.964			
^1F				0.918		
^1D					0.976	
^1P						0.952

The following three multiplets are most suitable for experimental observation:

$$3d\ ^3F^0 - 4f\ ^3G$$
$$^3D^0 - {}^3F$$
$$^3P^0 - {}^3D$$

A glance at the line intensity table shows that these three multiplets make up over 92% of the supermultiplet intensity. Within the experimental error, therefore, they make up almost the whole intensity of the triplet-supermultiplet. This was also found experimentally. It could be further shown that several of the intercombinations arising from the triplet-supermultiplet are negligible. The singlet-supermultiplet, on the other hand, gives rise to intercombinations that are comparable in intensity with the normal line.

The procedure just described makes it possible to use measurements made on a pure nitrogen plasma. This avoids the difficulties due to mixing, and the determination of the parameters of the plasma is very reliable. F 3 8

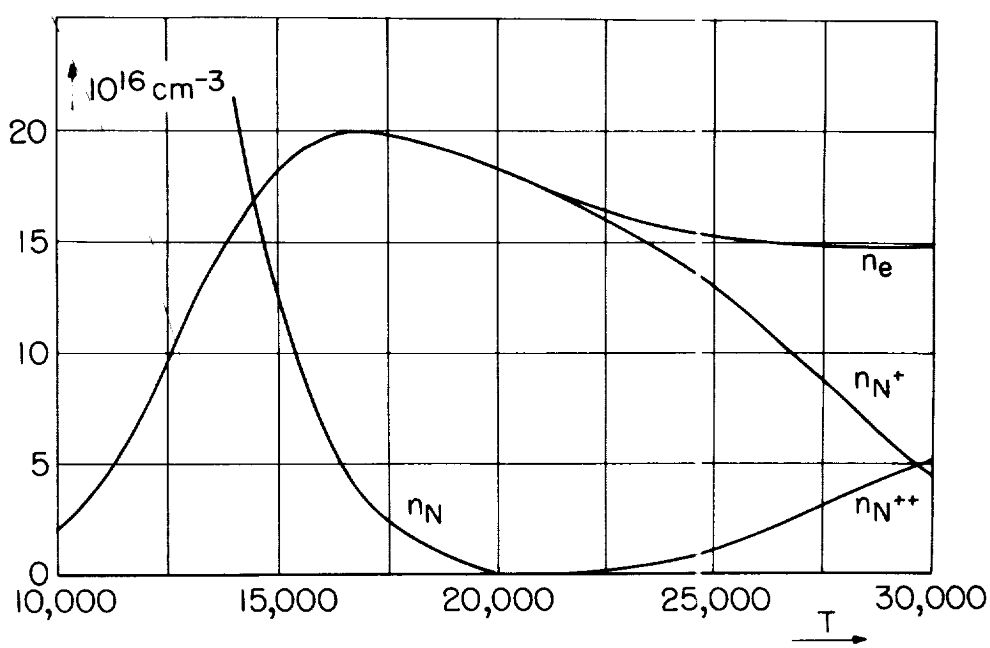
The following system of equations can be used to compute all the required quantities as functions of the temperature.

$$(1)\quad \frac{n_{N^+}}{n_N} = 2 \cdot \frac{Z(N^+)}{Z(N)} \cdot \frac{(2\pi m_e kT)^{3/2}}{n_e h^3} \cdot e^{-\frac{\chi_N - \Delta\chi}{kT}}$$

$$(2)\quad \frac{n_{N^{++}}}{n_{N^+}} = 2 \cdot \frac{Z(N^{++})}{Z(N^+)} \cdot \frac{(2\pi m_e kT)^{3/2}}{n_e h^3} \cdot e^{-\frac{\chi_{N^+} - \Delta\chi}{kT}}$$

$$(3)\quad \frac{P_0}{kT} = n_e + n_N + n_{N^+} + n_{N^{++}}; \qquad P_0 = 1.013 \cdot 10^6 \mathrm{dyn/cm}^2$$

$$(4)\quad n_e = n_{N^+} + 2n_{N^{++}}$$



Particle density of the nitrogen plasma (pressure = 1 atmosphere)

H. Maecker [11] has given the important details of a wall-stabilized arc suitable for use as a light source for producing a pure nitrogen plasma. A series of preliminary experiments led to several modifications, which finally made possible the production of the required temperature during a period of time sufficient for the experiment.

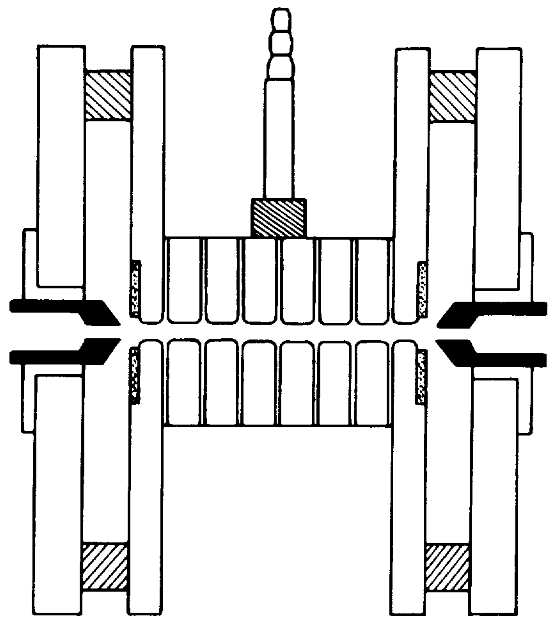


Diagram of the wall-stabilized arc

The spectrum was formed with a plane grating of dispersion 10 Å/mm. The measurement procedure was basically the same as that described in the preceding section. The lower dispersion and the wave length range which differed in part, required the use of the fine-grain Hauff plate Mikrosin with speed rating 12/10 DIN. Since the grating was stigmatic, the wedge could also be made with the same apparatus. The Euler standard lamp was again used, but this time was put directly in place of the arc.

The relative angular apertures of the arc and standard source were so chosen that the spectra they produced gave a photographic density in the same range. The calibration of the Zeiss step filter was carried out photoelectrically. A recording photometer was used to measure the density of the plates.

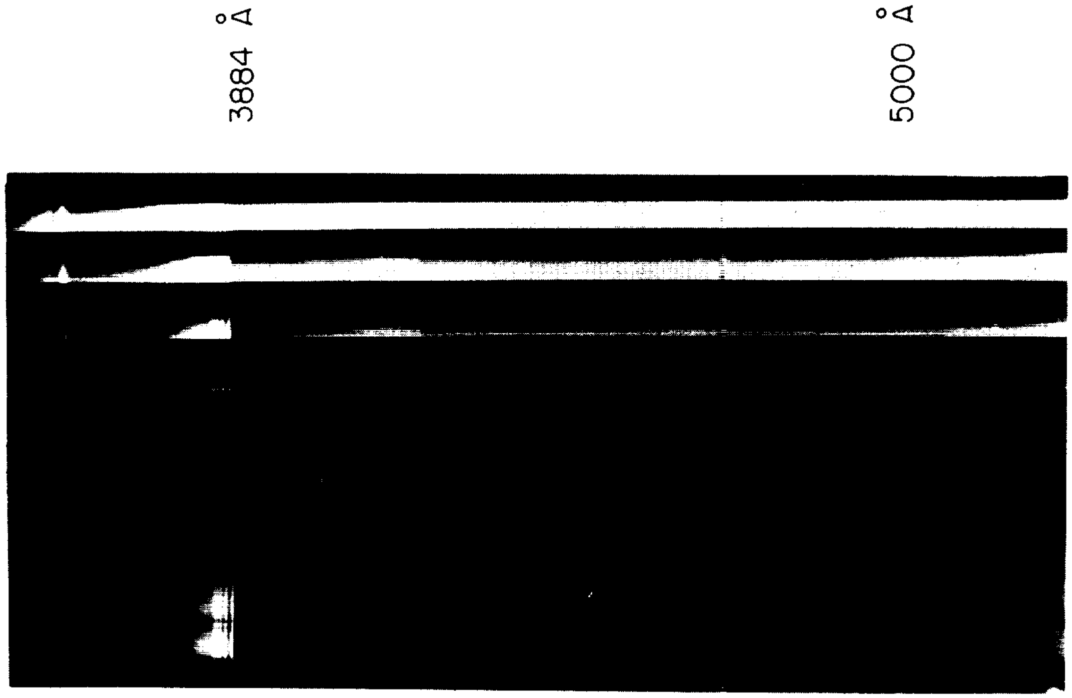
In this way, most of the N II lines lying between 3900 and 4900 Å were measured.

3. The helium-nitrogen mixture was prepared with a mixing apparatus. The desired components are mixed under high (10 to 40 atm) pressure above atmospheric. Using a pressure gauge with a precision of 0.6%, the desired partial pressures, when they are both large enough, can be determined to an accuracy of at least 1%.

Helium-nitrogen mixtures of different concentration ratios were investigated with the light source described in section III.2. To keep the arc off the copper segments, the individual plates must not be thicker than 5 mm, compared with 7 mm in pure nitrogen. Otherwise the arrangement was as in section III.2.

If it is assumed provisionally that the concentration ratios produced experimentally are maintained in the arc, the parameters of the plasma can be determined from the intensity of a helium line of known oscillator strength, with a known concentration ratio. In this way, the absolute oscillator strengths, obtained for N II by the method of section III.2 applied to the nitrogen plasma, might be checked.

The majority of the helium lines lying in accessible regions are not usable for our purpose. This is because, firstly the lines are too weak, and secondly the high electron pressure in the arc broadens the lines so much that even their tips only stand out faintly in the continuum.



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An example of a calibrated plate. Center, N II spectrum; top, 4 steps of the wedge; bottom, 2 exposures of the standard source.

Only three lines can be properly measured. These are

$$\lambda = 5876\ \text{Å}$$
$$\lambda = 5016\ \text{Å}$$
$$\lambda = 3889\ \text{Å}.$$

Of these the line at 5016 Å cannot be used since it overlaps with N II lines. Finally, therefore, only two helium transitions are left:

$$1s\,2p\ {}^3P^0 - 1s\,3d\ {}^3D,\ \lambda = 5876\ \text{Å}.$$
$$1s\,2s\ {}^3S\ - 1s\,3p\ {}^3P^0,\ \lambda = 3889\ \text{Å}.$$

In the literature the values given for the oscillator strengths of $\lambda = 5876$ Å are almost identical [1],but the values given for $\lambda = 3889$ show a marked disagreement.

However, the oscillator strength for $\lambda = 3889$ Å can easily be checked by a comparison with $\lambda = 5876$ Å. Since the two lines have very similar excitation energies, their oscillator strength ratio is proportional to their measured intensity ratio, and is independent of the temperature and other plasma parameters. The measurements gave a ratio:

$$\text{Measurement:} \quad \frac{f_{mn}^{5876}}{f_{mn}^{3889}} = 10.1$$

while the ratios from Biermann [1] and Allen's Tables "Astrophysical Quantities" are:

$$\text{Biermann:} \quad \frac{f_{mn}^{5876}}{f_{mn}^{3889}} = 6.7 \qquad \text{Allen:} \quad \frac{f_{mn}^{5876}}{f_{mn}^{3889}} = 9.7$$

A comparison shows that the values from Allen's [1] work are by far the closer to the measured values. We therefore used them for the subsequent computations:

$$f_{mn}^{5876} = 0.62 \qquad\qquad f_{mn}^{3889} = 0.064$$

The most suitable N II transitions are:

$$3s\ ^3P_1^0 - 3p\ ^3P_0\ ,\ \lambda = 4621\ \text{Å}$$
$$3p\ ^1P\ - 3d\ ^1D^0\ ,\ \lambda = 4447\ \text{Å}.$$

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According to the circumstances, one or other of these lines is used.

The investigations were carried out with mixtures of concentration ratios of helium to nitrogen of

1:1, 1:4, 1:10

The results obtained with the ratio 1:10 must be rejected, due to the weakness of the helium lines. For the two other concentration ratios, two and three different mixtures respectively were prepared and measured.

IV. Results

1. In this section the results of the absolute and relative measurements are brought together.

Measurements were made on the following multiplets:

By using the 3d-4f transitions in N II:

$3s\ ^3P^0 - 3p\ ^3P$
$3p\ ^3D\ - 3d\ ^3D^0$
$3p\ ^1P\ - 3d\ ^1D^0$
$3p\ ^1P\ - 3d\ ^1P^0$
$3d\ ^1F^0 - 4f\ ^1G$

By using the N II multiplet $3s\ ^3P^0 - 3p\ ^3P$:

$3s\ ^3P^0 - 3p\ ^3D$
$3s\ ^3P^0 - 3p\ ^3S$
$3p\ ^3D\ - 3d\ ^3F^0$
$3p\ ^3P\ - 3d\ ^3D^0$
$3p\ ^3S\ - 3d\ ^3P^0$

and the intercombinations:

$$3d\ ^3F_3^0 - 4f\ ^1G_4$$
$$3d\ ^1F_3^0 - 4f\ ^3G_4$$

The measurements on the spectrum of the water-stabilized arc gave the values:

TABLE 2

Spectrum	T	n_{N^+} cm^{-3}	n_e cm^{-3}
1	16800°	$12.22 \cdot 10^{16}$	$1.94 \cdot 10^{17}$
2	16600°	11.90	1.92
3	17000°	12.09	1.93
4	16850°	12.10	1.93
5	17000°	11.99	1.94

The parameters for the nitrogen plasma in the wall-stabilized arc, using the indicated multiplet, were:

TABLE 3

	Spectrum 1 T	Spectrum 2 T
3d $^3F^0$ - 4f ^3G	20280°	20580°
3d $^3D^0$ - 4f ^3F	20235°	20590°
3d $^3P^0$ - 4f ^3D	20405°	20640°

We see that the results show gratifying agreement among themselves.

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In the next Tables, the measured line strengths, oscillator strengths and σ^2-values [3] are presented with the values computed by the method of Bates and Damgaard [3]. All the measured multiplets and lines have the same upper term $1s^2\ 2s^2\ 2p\ (^2P^6)$. The line strength S [5] is as usual given in atomic units. σ^2 combines the relative with the absolute line strengths. Its meaning can be obtained from the paper of Bates and Damgaard. The multiplets are arranged according to the series and the supermultiplet.

TABLE 4 (ps-pp)

Measured values: Computed values:

σ^2 = values

Measured:

p · s \ p · p	^3D	^3P	^3S
^3P	5.4	5.5	4.5

Computed:

p · s \ p · p	^3D	^3P	^3S
^3F	4.8	4.8	4.8

Line strengths

Measured:

p · s \ p · p	^3D	^3P	^3S
^3P	81	49	13.4

Computed:

p · s \ p · p	^3D	^3P	^3S
^3P	72	44	14.5

Oscillator strengths

Measured:

p · s \ p · p	^3D	^3P	^3S
^3P	0.48	0.36	0.090

Computed:

p · s \ p · p	^3D	^3P	^3S
^3P	0.43	0.82	0.098

TABLE 5 (pp-pd)

σ^2 - values

Measured values:

p · p \ p · d	^3F	^3D	^3P	^1F	^1D	^1P
^3D	1.34	1.44				
^3P		1.34				
^3S			1.59			
^1D						
^1P					1.37	1.15
^1S						

Computed values:

p · p \ p · d	^3F	^3D	^3P	^1F	^1D	^1P
^3D	1.20	1.20	1.22			
^3P		1.31	1.30			
^3S			1.30			
^1D				1.48	1.38	1.50
^1P					1.16	1.18
^1S						1.73

Line strengths

Measured values:

p · p \ p · d	^3F	^3D	^3P	^1F	^1D	^1P
^3D	169	32				
^3P		91				
^3S			48			
^1D						
^1P					31	8.7
^1S						

Computed values:

p · p \ p · d	^3F	^3D	^3P	^1F	^1D	^1P
^3D	152	27	1.8			
^3P		89	29			
^3S			39			
^1D				62	10.4	0.75
^1P					26	8.8
^1S						17.3

Oscillator strengths

Measured values:

p · p \ p · d	^3F	^3D	^3P	^1F	^1D	^1P
^3D	0.68	0.14				
^3P		0.52				
^3S			0.91			
^1D						
^1P					0.70	0.22
^1S						

Computed values:

p · p \ p · d	^3F	^3D	^3P	^1F	^1D	^1P
^3D	0.62	0.114	0.0083			
^3P		0.51	0.181			
^3S			0.79			
^1D				0.57	0.079	0.0073
^1P					0.59	0.23
^1S						0.62

For the lines of the singlet-supermultiplet only two of the measurements were usable.

pd-pf

The computed line strengths for this series have already been given in section III.2 in the discussion of the measurement method.

Besides the triplet transitions used to determine the temperature, only two more lines in this series were investigated.

	Measured	Computed
$3d\ ^1F^0 - 4f\ ^1G$	$S = 70$ A.U.	$S = 95.7$ A.U.
$\lambda = 4530.4$ Å	$f_{mn} = 0.67$	$f_{mn} = 0.918$
$3d\ ^3F^0_3 - 4f\ ^1G_4$	$S = 26$ A.U.	
$\lambda = 4026.1$ Å	$f_{mn} = 0.28$	
$3d\ ^1F^0_3 - 4f\ ^3G_4$	$S = 32$ A.U.	
$\lambda = 4552.5$ Å	$f_{mn} = 0.30$	

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In order to compare the measured value for the singlet 4530 with theory, we must remember that, according to the J sum rule [5], in emission the line strength of the intercombination line $\lambda = 4026$ must be counted in. However, the sum of the two line strengths is:

$$\left.\begin{array}{ll} 4f\ ^1G_4 - 3d\ ^1F^0_3 & S = 70 \text{ A.U.} \\ 4f\ ^1G_4 - 3d\ ^3F^0_3 & S = 26 \text{ A.U.} \end{array}\right\} = 96 \text{ A.U.}$$

The sum agrees surprisingly well with the computed value.

In the next Table the measured and theoretical oscillator strengths and line strengths for the triplet lines are presented. For comparison between the relative line strength [5] and the measured value, the x_1 component was normalized to 100 in each case. The theoretical values of the relative line strength are valid for L-S coupling [5] (see Table 6, p. 15).

Since two complete multiplets were measured, except for a few weak lines, the values obtained can be checked by using the J sum rule. For some very weak lines theoretical values were substituted (see Tables 7-8, p. 16).

The measured line strengths are inserted in the scheme. By addition, the line strength sums are obtained for each row and column. If the relations required by the sum rule were strictly obeyed, the values in the next row or column would coincide with the measured values. In this next row or column, the statistically weighted theoretical sums themselves are introduced. With one exception, the measured sums agree with the theoretical sum rule values to within the experimental error. As a glance at the table shows, the one deviation is due to the line strength for $^3S_1 - {}^3P_2$ $\lambda = 5007.3$ Å, being too high.

Finally, we present some figures computed for the N II multiplet by a more elaborate method [2] than the one we used. Table 9 is taken from [2], with our measured values added. The σ^2-values of the multiplets are given in Table 9 (see p. 16).

The columns headed "Dipole velocity" and "Dipole length" refer to the calculation method used. For more details, [2] should be consulted. This method gives, as the Table shows, somewhat greater σ^2-values than that of Bates and Damgaard. This however brings them into better agreement with the measured values.

TABLE 6

Multiplet	Comp.	λ *	Meas. f_{mn}	B.D. f_{mn}	Meas. S_{rel}	L-S S_{rel}	Meas. S A.U.	B.D. S A.U.
$3s\ ^3P^0 - 3p\ ^3D$	2-3	5679.7	0.43	0.36	100	100	40	33.4
	1-2	5666.6	.35	.32	48	53.6	19.6	17.9
	0-1	5676.0	.45	.42	21	23.8	8.5	7.94
	2-2	5710.8	.059	.063	13.6	17.9	5.6	5.95
	1-1	5686.2	.11	.103	15.5	17.9	6.4	5.95
	2-1	5730.7	-----	.0042	-----	1.2	-----	.40
$3s\ ^3P^0 - 3p\ ^3P$	2-2	4630.5	0.29	0.24	100	100	22	18.1
	1-1	4613.9	.067	.080	13.9	20	3.1	3.62
	2-1	4643.1	.10	.079	33.7	33.4	7.4	6.05
	1-0	4621.4	.10	.106	21.3	26.8	4.7	4.84
	1-2	4601.5	.15	.133	32.0	33.4	7.0	6.05
	0-1	4607.2	.35	.32	24.1	26.8	5.3	4.84
$3s\ ^3P^0 - 3p\ ^3S$	2-1	5045.1	0.089	0.097	100	100	7.4	8.05
	1-1	5010.6	.095	.098	64	60	4.7	4.83
	0-1	5002.7	.089	.098	20	20	1.5	1.61
$3p\ ^3D - 3d\ ^3F^0$	3-4	5005.1	0.62	0.57	100	100	71	65.2
	2-3	5001.5	.64	.55	68	69.1	52	45
	1-2	5001.1	.72	.62	46	46.7	35	30.4
	3-3	5025.7	.047	.049	7	8.8	5.4	5.65
	2-2	5016.4	.071	.069	7.5	8.8	5.8	5.65
	3-2	5040.8	-----	.0014	-----	.2	-----	.16
$3p\ ^3P - 3d\ ^3D^0$	2-3	5941.7	0.46	0.43	100	100	45	41.6
	1-2	5931.8	.37	.38	49	53.6	22	22.2
	0-1	5927.8	.53	.51	23	23.8	10.3	9.9
	2-2	5952.4	.069	.076	15	17.9	6.7	7.41
	1-1	5940.3	.11	.126	14	17.9	6.5	7.41
	2-1	5960.9	-----	.005	-----	1.2	-----	.49
$3p\ ^3S - 3d\ ^3P^0$	1-2	5007.3	0.57	0.44	100	100	28	21.6
	1-1	4994.4	.31	.26	57	60	16	13.0
	1-0	4987.4	.091	.088	16	20	4.5	4.33
$3p\ ^3D - 3d\ ^3D^0$	3-3	4803.3	0.12	0.101	100	100	13.4	11.2
	2-2	4788.1	.095	.080	56	55.8	7.5	6.26
	1-1	4779.7	.097	.086	34	36.2	4.6	4.05
	3-2	4810.3	.012	.013	9.9	12.5	1.33	1.4
	2-1	4793.7	.019	.017	11.1	12.1	1.49	1.35
	2-3	4781.2	-----	.018	-----	12.5	-----	1.4
	1-2	4774.2	.023	.029	8.0	12.1	1.1	1.35

*C. E. Moore, A Multiplet Table of Astrophysical Interest, Princeton, New Jersey, (1945).

TABLE 7 (ps-pp)

	$^3P_0$	$^3S_1$	$^3P_1$	$^3D_1$	$^3P_2$	$^3D_2$	$^3D_3$	ΣS		
$^3P_0$		1.5	5.3	8.5				15.3	15.7	1
$^3P_1$	4.7	4.7	3.1	6.4	7.0	19.6		45.5	47.1	3
$^3P_2$		7.4	7.4	0.4	22	5.6	40	83.0	78.4	5
ΣS	4.7	13.6	15.8	15.3	29	25.2	40	meas.	theor.	2_J + 1
	5.2		15.5		25.8		36.2	theor.		
	1		3		5		7	2_J + 1		

TABLE 8 (pp-pd)

	$^3P_0$	$^3P_1$	$^3D_1$	$^3P_2$	$^3D_2$	$^3F_2$	$^3D_3$	$^3F_3$	$^3F_4$	ΣS		
$^3P_0$		3.3	10.3							13.6	13.5	1
$^3S_1$	4.7	16		28						48.7		
$^3P_1$	3.3	2.4	6.5	4.1	22					38.3	40.5	3
$^3D_1$	0.2	0.2	4.6	----	1.1	35				41.1		
$^3P_2$		4.1	0.5	12.2	6.7		45			58.5	67.5	5
$^3D_2$		0.5	1.5	0.2	7.5	5.8	1.7	52		59.2		
$^3D_3$				0.9	1.3	0.2	13.4	5.4	71	92.4	94.5	7
ΣS	8.2	26.5	23.5	45.4	38.5	41	60.1	57.4	71	meas.	theor.	2_J + 1
	8.2	24.6			41		57.4		73.8	theor.		
	1	3			5		7		9	2_J + 1		

TABLE 9

σ^2-value:

	Dipole length	Dipole velocity	Coulomb Approx.	Meas. value
3p ^3D - 3d $^3F^0$	1.30	1.27	1.20	1.34
3p ^3D - 3d $^3D^0$	1.34	1.27	1.20	1.44
3p ^3P - 3d $^3D^0$	1.47	1.76	1.32	1.34

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The Errors

The experimentally determined error of the relative oscillator strengths was

$$\frac{\Delta\left(f^{II}/f^{I}\right)}{f^{II}/f^{I}} = 6\%$$

For the relative error of the absolute oscillator strength f^{II}, measured in a pure nitrogen plasma at T = 20,000 degrees, the exact theory of the errors gives:

$$\frac{\Delta f_{mn}^{II}}{f_{mn}^{II}} = \frac{\Delta\left(J^{II}/J^{I}\right)}{J^{II}/J^{I}} + \frac{1}{4.74}\frac{\Delta J^{I}}{J^{I}} + \frac{1}{4.74}\frac{\Delta l}{l} + 0.79\,\frac{\Delta f_{mn}}{f_{mn}^{I}}$$

Here $\Delta f^{I}/f^{I}$ is the relative error of the oscillator strength for the transition in question, 3d-4f.

If, taking the worst case, we put the absolute measurement error, $\Delta J^{I}/J^{I} = 20\%$, the error in the emitting layer length $\Delta l/l = 10\%$, and the experimentally determined error of the relative oscillator measurement

$$\frac{\Delta\left(J^{II}/J^{I}\right)}{J^{II}/J^{I}} = 6\% \qquad \text{we get} \qquad \frac{\Delta f_{mn}^{II}}{f_{mn}^{II}} = 12\% + 0.8\,\frac{\Delta f_{mn}^{I}}{f_{mn}^{I}}$$

Considering that in practice the total intensity of the supermultiplet was used for the reduction of the results, the actual error should not exceed

$$\frac{\Delta f_{mn}^{I}}{f_{mn}^{I}} = 10\%$$

This would lead to a total error $\Delta f_{mn}^{II}/f_{mn}^{II}$ of from 12 to 20%.

2. The nitrogen-helium mixture. In the following section the results of the measurement on the nitrogen-helium mixture will be considered from two points of view.

a) If a constant given concentration ratio is assumed, the intensity of a helium line can be used to compute the parameters of the plasma. The N II intensities then give the N II oscillator strengths given in Table 10. The third column gives the measured values from Table 6, and the last column the oscillator strengths computed from the Bates and Damgaard method.

TABLE 10

λ (Å)	N-He-Plasma f_{mn}	N-Plasma f_{mn}	Calculated from B.D. f_{mn}
4621	0.053	0.10	0.11
4447	.36	.70	.59
3d $^3F^0$ - 4f ^3G	.29	----	.83

We see that the oscillator strengths obtained are two to three times smaller than those from the previous measurements. This result is especially noticeable for the 3d-4f transition.

b) The differences between the oscillator strengths obtained for N II from the nitrogen plasma and the helium-nitrogen mixture are much too great to explain by experimental errors. An explanation of these inconsistent experimental results seems at first a matter of considerable difficulty. The contradiction can be explained, however, if we suppose that in the hot axis of the arc the concentration ratio of nitrogen to helium is different from the originally measured value. The experiment points to an increase of the helium concentration in the hot arc axis.

If we rely on the N II oscillator strengths obtained from the pure nitrogen plasma and the theoretical helium values, we can determine spectroscopically the helium concentration on the axis of the arc. If the helium concentration as originally mixed is designated c_0, and that found spectroscopically on the arc axis c', we get for the change in concentration

$$\Delta c = c' - c_0,$$

and we have given the values of this quantity in the following Table 11.

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TABLE 11

Mixture	Temperature	Concentration c_0	Expected conc. ratio He:N	Measured Δc	Measured concentration ratio He:N
I	19080°	0.50	1	0.154	1.89
II	18570°	.20	0.25	.085	.40

The explanation of this separation by thermal diffusion, which is the most probable hypothesis, will not be taken up due to the considerable theoretical difficulties.

V. Summary

Several oscillator strengths for ionized nitrogen have been measured, by relating them to the hydrogen-like triplet-multiplet of the N II series 2p3d-2p4f; the oscillator strengths were calculated by the method of Bates and Damgaard. It was found that the Bates and Damgaard Coulomb field approximation gave correct oscillator strengths, to within, generally, 20% for the measured N II lines of the series

$$1s^2\ 2s^2\ 2p(^2P^0) \qquad \begin{matrix} 3s - 3p \\ 3p - 3d \end{matrix}$$

For the most part, the experimental values for these series lay from 10 to 20% above the theoretical values.

The attempt to verify the oscillator strengths obtained in pure nitrogen by measurements in a helium-nitrogen mixture, using the known helium oscillator strengths, failed. The results of the measurements lead us to suppose that there is a considerable change in the concentration of the components of a gas mixture in the plasma of a wall-stabilized arc.

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Signed Frithjof Mastrup

I hereby declare under oath that this work is my own in form and content, apart from the advice of my academic director. The references I used are given. The work has not already been presented either in part or in whole as a thesis, and has not yet been published.

Kiel, October 3, 1957

Signed Frithjof Mastrup

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